WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Air Toxics Monitoring Quality Assurance Project Plan

Air Quality Program

September 2004

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Air Toxics Monitoring Quality Assurance Project Plan

Air Quality Program

Prepared by:
Stan Rauh
Washington State Department of Ecology
Air Quality Program

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1 QA Plan Identification and Approval

Title: Air Toxics Monitoring Quality Assurance Project Plan for the State of Washington Department of Ecology Air Quality Program

The Air Toxics Monitoring Quality Assurance Project Plan for the Air Quality Program is recommended for approval and commits the Program to follow the elements described within.

____________________________________ Date: ___________
Mary Burg, Air Quality Program Manager

____________________________________ Date: ___________
Mike Ragan, Air Monitoring Coordinator

____________________________________ Date: ___________
John Williamson, Air Toxics Project Coordinator

____________________________________ Date: ___________
Stan Rauh, Quality Assurance Coordinator

____________________________________ Date: ___________
Cliff Kirchmer, Ecology QA Manager

EPA Region 10

____________________________________ Date: ___________
Roy Araki, Quality Assurance Manager

____________________________________ Date: ___________
Keith Rose, Air Program Oversight Manager

2 Distribution

A copy of the Air Toxics Monitoring Quality Assurance Project Plan is distributed to the following listed below:

Name	Position	Organization
Mary Burg	Air Quality Program Manager	Ecology
Phyllis Baas	Technical Services Section Manager	Ecology
Mike Ragan	Air Monitoring Coordinator	Ecology
Stan Rauh	Air Monitoring QA Coordinator	Ecology
Doug Brown	Northwest Regional Office (NWRO) Regional Supervisor	Ecology
John Williamson	Air Toxics Project Coordinator	Ecology
Cliff Kirchmer	Ecology QA Officer	Ecology
James Frost	Air Monitoring Operator	Ecology
Doug Knowlton	Air Monitoring Operator	Ecology
Dr. Hal Westberg	Air Toxics Laboratory Project Officer, WSU	Washington State University
Keith Rose	Regional project Officer	USEPA Region 10
Roy Araki	Regional QA Manager	USEPA Region 10

3 Organization and Responsibilities

3.1 Roles and Responsibilities

Federal, State, Tribal and local agencies all have important roles in developing and implementing satisfactory air monitoring programs. As part of the planning effort, EPA is responsible for developing National Ambient Air Quality Standards (NAAQS), and identifying a minimum set of QC samples from which to judge data quality. The State and local organizations are responsible for taking this information and developing and implementing a quality system that will meet the data quality requirements. Then, it is the responsibility of both EPA and the State and local organizations to assess the quality of the data and take corrective action when appropriate. The responsibilities of each organization follow.

3.2 Washington State Department of Ecology Air Quality Program (Ecology)

40 CFR Part 58 defines a State Agency as "the air pollution control agency primarily responsible for the development and implementation of a plan under the Clean Air Act (CAA)". Section 302 of the CAA provides a more detailed description of the air pollution control agency.

40 CFR Part 58 defines the Local Agency as "any local government agency, other than the state agency, which is charged with the responsibility for carrying out a portion of the plan (SIP)."

The major responsibility of State and local agencies is the implementation of a satisfactory monitoring program, which includes the implementation of an appropriate quality control and quality assurance program. It is the responsibility of State and local agencies to implement quality assurance programs in all phases of the environmental data operation (EDO), including the field, their own laboratories, and in any consulting and contractor laboratories

The title and responsibilities of key personnel are:

Air Quality Program Manager – Mary Burg

- Management of the Air Quality Program

Technical Services Section Manager – Phyllis Baas

- Calibration and Quality Control Standards
- Air Monitoring Equipment Procurement, Testing, and Calibration
- Parts and Supplies Inventory
- Major Equipment Repair
- Telemetry System Operation and Maintenance
- Site, Shelter and Utility Contracts
- AQS Data Submittals

Air Quality Program Quality Assurance Coordinator – Stan Rauh

- Air Monitoring Procedures and Training
- Quality Assurance Policies, Plans, and Procedures
- Performance and System Audits
- Final Data Validation

NWRO Regional Section Supervisor – Doug Brown

- Coordinate and Oversee Regional Monitoring Activities
- Supervise Regional Air Monitoring Station Operators

Air Toxics Project Coordinator – John Williamson

- Network Evaluation and Design Coordination
- Station Installation and Operation Coordination
- Air Toxics Data Management
- Final Reports

Ecology Quality Assurance Officer – Cliff Kirchmer

- Oversees Ecology QA Activities
- Reviews and Approves the QAPP

Air Monitoring Station Operators

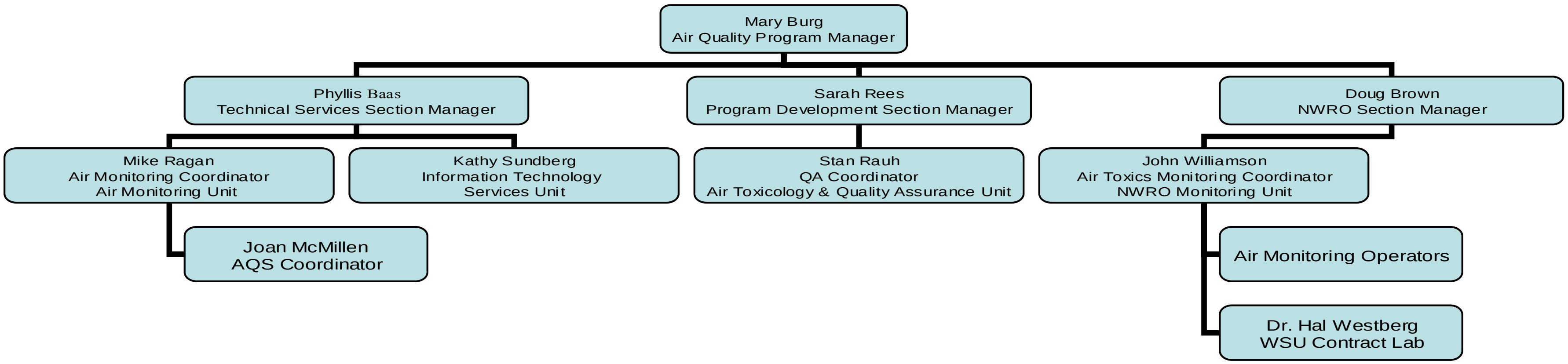
- Station Installation, Operation, Sample Collection
- Sample Shipments to WSU
- Quality Control and Precision Checks
- First Level Data Validation
- Routine Maintenance and Repair

WSU Contract Laboratory Manager – Dr. Hal Westberg

- Laboratory Quality Assurance Policies, Plans, and Procedures
- Verifying All Laboratory QA Activities
- Canister and Tube Preparation and Certification
- Canister and Tube Shipping to Monitoring Sites
- Receipt, Inspection, Equilibration, Pre/post weighing and Shipment of PM_{10} Filters to Monitoring Sites
- Shipping of Weighed and Cut PM_{10} Filters to Energy Northwest Environmental Sciences Laboratory (ENES)
- Analysis of VOCs, Carbonyls, and Metals
- Assessing and Reporting Data Quality
- Data validation of analytical data (VOCs, Carbonyls, and Metals)
- Inter and Intra Laboratory Testing
- Storage and Archive of Hardcopy Laboratory Data and Documentation
- Delivery of Electronic Data Reports to Information Management Supervisor
- Flagging and Reporting Suspect Data to the Quality Assurance Coordinator
- Storage and Archive of Electronic Data
- Preparing and Delivering Reports to the Air Toxics Monitoring Coordinator

Figure 1 represents the organizational structure of the areas of the Air Quality Program that are responsible for the activities defined above.

Figure 1 Air Quality Program Organizational Chart



3.3 Washington State University (WSU)

Under contract to the Washington State Department of Ecology's Air Quality Program Washington State University is the primary contractor for the analysis of Volatile Organic Compounds (VOCs) and Carbonyls. Dr Hal Westberg directs all activities at the contract laboratory. Under contract to WSU is ENES which will perform the metals analysis of the PM_{10} filters.

3.4 EPA Office of Air Quality Planning and Standards (OAQPS)

OAQPS is the organization charged under the authority of the Clean Air Act (CAA) to protect and enhance the quality of the nation's air resources. OAQPS sets standards for pollutants considered harmful to public health or welfare and, in cooperation with EPA's Regional Offices and the States, enforces compliance with the standards through state implementation plans (SIPs) and regulations controlling emissions from stationary sources. OAQPS evaluates the need to regulate potential air pollutants, especially air toxics and develops national standards; works with State, Local and Tribal (S/L/T) agencies to develop plans for meeting these standards. In addition, OAQPS provides the funding, through the CAA Section 103 and 105 funds.

Within the OAQPS Emissions Monitoring and Analysis Division (EMAD), the Monitoring and Quality Assurance Group (MQAG) is responsible for the oversight of the NATTS. MQAG has the following responsibilities:

- Ensuring that the methods and procedures used in making air pollution measurements are adequate to meet the programs objectives and that the resulting data are of satisfactory quality;
- Evaluating the performance, through Technical Systems Audits (TSAs) and Management System Reviews (MSRs), of organizations making air pollution measurements;
- implementing satisfactory quality assurance programs over EPA's Ambient Air Quality Monitoring Network;
- Ensuring that national regional laboratories are available to support toxics and QA programs;
- Rendering technical assistance to the EPA Regional Offices and air pollution monitoring community.

3.5 EPA Region 10

The EPA Regional Offices will address environmental issues related to the States within their jurisdiction and to administer and oversee regulatory and congressionally mandated programs. The major quality assurance responsibilities of EPA's Regional Offices, in regards to the National Air Toxics Trends Sites (NATTS), are the coordination of quality assurance matters at the Regional levels with the State and local agencies. This is accomplished by the designation of EPA Regional Project Officers who are responsible for the technical aspects of the program including:

- Reviewing QAPPs by Regional QA Officers who are delegated the authority by the Regional Administrator to review and approve QAPPs for the Agency;

- Supporting the air toxics audit evaluation program;
- Evaluating quality system performance, through TSAs and network reviews whose frequency is addressed in the Code of Federal Regulations;
- Acting as a liaison by making available the technical and quality assurance information developed by EPA Headquarters and the Region to the State and local agencies including making EPA Headquarters aware of the unmet quality assurance needs of the State and local agencies.

4 Problem Definition and Background

4.1 Problem Statement and Background

4.1.1 Background

There are currently 188 hazardous air pollutants (HAPs), or air toxics, regulated under the CAA that have been associated with a wide variety of adverse health effects, including cancer, neurological effects, reproductive and developmental effects, as well as ecosystem effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics. While in some cases the public may be exposed to an individual HAP, more typically people experience exposures to multiple HAPs and from many sources. Exposures of concern result not only from the inhalation of these HAPs, but also, for some HAPs, from multi-pathway exposures to air emissions.

4.1.2 The National Air Toxics Trends Stations and the Role of the AQP

EPA finalized the Urban Air Toxics Strategy (UATS) in the Federal Register on July 19, 1999. The UATS states that emissions data are needed to quantify the sources of air toxics impacts and aid in the development of control strategies, while ambient data are needed to understand the behavior of air toxics in the atmosphere after being emitted. Since ambient measurements cannot practically be made everywhere, modeled estimates are needed to extrapolate our knowledge of air toxics impacts into locations without monitors. Exposure assessments, together with health effects information, are then needed to integrate all of these data into an understanding of the implications of air toxics impacts and to characterize air toxics risks. The EPA proposed the National Air Toxics Assessment (NATA) to meet this need. There are four activities which are key to the success of the NATA.

- Source-specific standards and sector-based standards, including section 112 standards, i.e., Maximum Achievable Control Technology (MACT), Generally Achievable Control Technology (GACT), residual risk standards, and section 129 standards.
- National, regional, and community-based initiatives to focus on multi-media and; cumulative risks, such as the Integrated UATS, Great Waters, Mercury initiatives, Persistent Bio-accumulative Toxics (PBT) and Total Maximum Daily Load (TMDL) initiatives, and Clean Air Partnerships;
- NATA activities that will help EPA identify areas of concern, characterize risks and track progress. These activities include expanded air toxics monitoring, improving and

periodically updating emissions inventories, national- and local scale air quality and exposure modeling, and continued research on effects and assessment tools, leading to improved characterizations of air toxics risk and reductions in risk resulting from ongoing and future implementation of air toxics emissions control standards and initiatives;
- Education and outreach.

The success of the NATA critically depends on our ability to quantify the impacts of air toxics emissions on public health and the environment. All of these activities are aimed at providing the best technical information regarding air toxics emissions, ambient concentrations, and health impacts to support the development of sound policies for NATA. Specifically, these activities include:

- The measurement of air toxics emission rates from individual pollution sources;
- the compilation of comprehensive air toxics emission inventories for local, State, and national domains;
- The analysis of patterns and trends in ambient air toxics measurements;
- The estimation of ambient air toxics concentrations from emission inventories using dispersion modeling;
- The estimation of human and environmental exposures to air toxics, and;
- The assessment of risks due to air toxics;
- **The measurement of ambient concentrations of air toxics at trends monitoring sites throughout the nation.**

Analysis was performed by OAQPS to ascertain the size and features of a national trends network that would satisfy the goals as stated above. This analysis illustrated that a number urban and rural locations would provide the needed coverage for estimates of national trends. The Air Quality Program (AQP) was contacted by the EPA to support one of these national trends sites. The AQP has agreed to provide the support to this network known as the National Toxics Air Trends Sites or NATTS. The AQP will support one monitoring station as agreed through the Section 103 and 105 funds received from the Regional Office.

This QAPP focuses on the Quality Assurance (QA) and Quality Control (QC) that will be instituted by the AQP to fulfill its obligation. In order to better focus the data collection activities on the final use of the data, a DQO process was performed in Chapter 6 of this QAPP.

4.2 List of Pollutants

There are 33 urban air toxics identified in the draft Integrated Urban Air Toxics Strategy (UATS). They are a subset of the 188 toxics identified in Section 112 of the CAA which are thought to have the greatest impact on the public and the environment in urban areas. The AQP staff reviewed the 33 air toxics list and consulted with EPA staff. After several consultations, a final list of compounds was selected. The list is based on 2 key limitations taken from the EPA's Concept Paper:

- A major portion of the 33 Unified Air Toxics Strategy (UATS) pollutants can be measured with 3 field and lab systems;
- The limitations of the State-of-the-Science instruments.

A number of compounds on the UATS list are difficult to characterize or the methods have not been developed yet. These compounds will not be included in the pollutant list. If at some time in the future methods are developed for these compounds, the AQP may, include these compounds. The AQP will report to the national Air Quality System (AQS) as many compounds as possible listed in the "Core" section of Table 4.1. Since the collection and analysis of samples will also provide data on other compounds, the AQP will report values to AQS that can be quality assured and validated by the procedures detailed in this QAPP.

Table 4.1 List of Air Toxics

Core	Max
Benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,2-dichloropropane, dichloromethane, tetrachloroethylene, trichloroethylene, vinyl chloride, arsenic, beryillium, cadmium, chromium, lead, manganese, formaldehyde and acrolein	Acrylonitrile, benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,2 dibromomethane, 1,3-dichloropropene, 1,2-dichloropropane, ethylene dichloride, ethylene oxide, dichloromethane, tetrachloro ethane, tetrachloroethylene, trichloroethylene, vinyl chloride, arsenic, beryillium, cadmium, chromium, lead, mercury, manganese, nickel, acetaldehyde, formaldehyde and acrolein, 2,2,7,8 tetrachlorobenzo-p-dioxin, coke oven emissions, hexachlorobenzene, hydrazine, polycyclic organic matter, polychloronated biphenyls, quinoline

As can be seen from Table 4.1, there are a number of additional air toxics in the Max list. Many of these are air toxics that the current analytical systems can measure. The AQP will report the compounds that are on the Core and Max list if these can be detected and analyzed while collecting the data on the required list.

4.3 Locations of Interest for HAPS

The main objective for the AQP NATTS is to provide data for the national trends, as determined in Chapter 6 of this QAPP. However, the AQP may also operate other air toxics monitoring stations to characterize general exposure and temporal and spatial variability. Further information on air toxics is needed from other cities and both industrial/downtown and suburban areas within Washington. The AQP has decided to target these areas in addition to the NATTS for future monitoring as funding becomes available.

5 Project/Task Description

5.1 Description of Work to be Performed

The measurement goal of the NATTS is to estimate the concentration, in units of micrograms per cubic meter (ug/m^3) and parts per billion/volume (ppbv) of air toxic compounds of particulates and gases. This is accomplished by three separate collection media:

- canister sampling with passivated canisters;
- 2,4-Dinitro-phenyl hydrazine (DNPH) cartridges;
- Particulate Matter – 10 micron (PM_{10}) high volume sampling on an 8 x 10" quartz glass filter;
- and diesel emissions through continuous spectrophotometry.

5.2 Field Activities

Table 5.1, 5.2, 5.3 and 5.4 summarizes some of the critical performance requirements.

Table 5.1 Design/Performance Specifications - PM_{10} - Toxic Metals

Equipment	Frequency	Acceptance Criteria
Filter Design Specs. Size Medium Filter thickness Collection efficiency	1 in 6 days	8.5" x 11" Quartz Glass Fiber Filter 0.50 mm 99.95%
Sampler Performance Specs. Sample Flow Rate Flow Regulation Flow Rate Precision Flow Rate Accuracy Clock/Timer	1 in 6 days	1.13 m^3/min. 0.1 m^3/min. $\pm$7% $\pm$7% 24 hour $\pm$ 2 min accuracy

Table 5.2 Design/Performance Specifications - Air Canister Sampler - Volatile Organic Compounds

Equipment	Frequency	Acceptance Criteria
Canister Design Specs. Size Medium Max Pressure Max. pressure drop Collection efficiency Lower Detection Limit	1 in 6 days	6 liters spherical Passivated SUMMA electro-polished Stainless Steel Canister 30 psig 14 psig. 99% compound specific, usually >0.1 ppbv
Sampler Performance Specs. Sample Flow Rate Flow Regulation Flow Rate Precision Flow Rate Accuracy External Leakage Internal Leakage	1 in 6 days	180 cc/min. 1.0 cc/min. $\pm$10% $\pm$10% Vendor specs Vendor specs 24 hour $\pm$ 2 min accuracy

Table 5.3 Design/Performance Specifications - Carbonyl Sampler - Aldehyde and Ketone Compounds

Equipment	Frequency	Acceptance Criteria

Equipment	Frequency	Acceptance Criteria
Filter Design Specs. Size Medium	1 in 6 days	100 mm Cylindrical Silica Gel cartridge coated with 2,4-Dinitro-phenyl hydrazine
Sampler Performance Specs. Sample Flow Rate Flow Regulation Flow Rate Precision Flow Rate Accuracy External Leakage Internal Leakage Clock/Timer	1 in 6 days	0.20 m^3/min. 0.2 m^3/min. $\pm$10% $\pm$10% Vendor specs Vendor specs 24 hour $\pm$ 2 min accuracy

Table 5.4 Design/Performance Specifications – Aethalometer – Black and Organic Carbon

Equipment	Frequency	Acceptance Criteria
Sampler Performance Specs. Sample Flow Rate Size medium Data Recording Power Temperature Range Wavelength Time Resolution Sensitivity	Continuous Continuous	2 to 6 l/min. 19” by 10.5 “ Quartz Tape 0-5 VDC 60 watts/ 110V AC 0 – 40 deg. C 880 nm and 370 nm 1hour or 1minute 0.1 ug/m3

The AQP assumes the sampling instruments to be adequate for the sampling for air toxics. All of the instruments operated in the field are vendor supplied. The descriptions of the samplers are similar to the instruments described in the references noted above.

5.2.1 Field Measurements

Table 5.1, 5.2, 5.3 and 5.4 represents the field measurements that will be collected. These tables are presented in the “Compendia of Organic and Inorganic Methods.” At the urging of the EPA, the AQP will also measure Elemental Carbon (EC) and Organic Carbon (OC) using the Aethalometer. This is a continuous instrument that draws samples through quartz tape. The OC/EC particles are trapped on the tape and analyzed via spectrophotometry at 880 and 370 nm. The data are stored on the internal 3.5 inch drive and can be retrieved during site visits. All other instruments collect discreet data and are stored in the instrument for downloading by the field operator during routine visits.

5.3 Laboratory Activities

All laboratory activities in support of the Air Toxics Monitoring Project are supervised by Dr. Hal Westberg at Washington State University (Dept. of Civil and Environmental Engineering). VOC analyses will be performed in the Laboratory for Atmospheric Research (WSU-LAR) at

Washington State University. Metals from PM_{10} collections will be determined at Energy Northwest's Environmental Laboratory in Richland Washington.

5.3.1 Pre-sampling Preparation

- **PM$_{10}$:** High purity quartz microfibre filters for use in PM_{10} samplers have been shipped by EPA to WSU. Prior to shipment EPA had one of their contractors determine metal reside on this particular lot (30 filters selected at random, acid extraction with microwave heating, analysis by ICP). WSU personnel will visually inspect each filter for defects prior to use. The LAR has a room dedicated for gravimetric analysis. It contains the microbalance (Mettler H20), constant humidity chamber (Scienceware Dry-Keeper), and hydrothermograph (Science Associates) and filter storage cabinets. After filters have been equilibrated and weighed, they will be individually labeled in plastic bags for transport to Ecology's NWRO in Bellevue. WSU has a contract with Quality Control Services, Inc for servicing and calibration of analytical balances. In addition, we routinely check balance integrity with a NIST certified weight set.
- **VOC:** Sampling canisters purchased from commercial suppliers are transported to WSU for cleaning and evacuation prior to field deployment. Cleaning and certification procedures are performed in accordance with the method guidelines. Canisters are shipped in cardboard boxes by Federal Express. Canisters are stored at WSU-LAR when waiting to be analyzed and after cleaning prior to field deployment. In the field pressure measurements prior to and following sample collection are made to check sample integrity. Post sample canister pressures are confirmed when they arrive at WSU.
- **Carbonyl:** Silica cartridges pre-coated with DNPH are shipped by the vendor directly to Ecology. Each cartridge is individually wrapped and marked with a Lot number. Three cartridges from each Lot are shipped to WSU for certification. Formaldehyde and acetaldehyde levels on the blank cartridges must be below levels described in method TO-11A and subsequent guidance documents. After deployment in the field samplers, the capped cartridges are placed in screw top bottles to which has been added a filter strip impregnated with DNPH. The exposed cartridges are shipped to WSU-LAR for analysis.

Shipping/Receiving

Shipping of filters, canisters and carbonyl cartridges between the analytical laboratory and NWRO is accomplished through Federal Express. Samples collected in the field are labeled individually and recorded in a logbook. A photocopy of the field log accompanies each sample during transit. Upon arrival at WSU-LAR, the samples are logged in and stored for analysis. Following gravimetric analysis, the PM_{10} filters will be sectioned into 1.0 in. strips as described in Compendium Method IO-3.1. Several strips from each filter will be packaged in a plastic bag and paper envelope for transfer to the Energy Northwest Laboratory in Richland. Shipping from Pullman to Richland will be accomplished via a WSU intercampus courier service. Carbonyl cartridges are shipped under ambient conditions in the containers describe previously. Upon arrival at WSU-LAR, the cartridges are stored in a cold room.

Post-Sampling:

- Upon arrival at WSU-LAR, each filter will be logged in and examined for physical defects. Filters will be equilibrated in the humidity chamber for 24 hr and then weighed. Filters then will be cut into strips in preparation for metals analysis. All handling and cutting of filters will be performed as described in Compendium Method IO-3.1. Energy Northwest will log in the filter strips and extract the metals for analysis using procedures outlined in Compendium Method IO-3.5 and the TPMS guidelines document.
- VOC determinations will be performed at WSU-LAR using GC with FID and ECD procedures (TO-14). At the start of the program, a few canister samples will be run on a GC/MS system to confirm peak assignments and to ensure target compound peaks are interference free.
- The DNPH derivatives of formaldehyde and acetaldehyde are eluted from the carbonyl cartridges and analyzed as described in Method TO-11A. These determinations are performed in the WSU-LAR.
- Raw data from the analytical instruments will be converted to concentrations for the "core" compounds using algorithms developed from calibration experiments and known air sample volumes. Data reduction and interpretation will be established through manual examination of the calculated concentration of each individual compound. When concentrations fall outside an acceptable range they are flagged and WSU will determine whether or not an analytical problem exists. This is done by examining the chromatogram for interference from a closely eluting compound and/or peak integration problems. In addition, WSU looks at the sample as a whole to see if all compounds exhibit elevated concentrations. The data validity decision is made by Dr. Westberg.
- WSU-LAR will tabulate all of the analytical data in electronic format. When QA assessments are completed, the species designated for reporting will be transformed into the Air Quality System (AQS) format and sent to Ecology. Ecology personnel will review the data and distribute it as they deem appropriate (i.e., to the national AQS data base, local agencies, etc.).

Analytical data (chromatograms, raw data files, final data reports, etc.) acquired will be archived as electronic files at WSU-LAR. WSU-LAR will archive unextracted PM_{10} filter strips.

5.4 Project Assessment Techniques

An assessment is an evaluation process used to measure the performance or effectiveness of a system and its elements. As used here, assessment is an all-inclusive term used to denote any of the following: performance evaluation (PE), MSRs, TSAs, peer review, inspection, or surveillance. Section 18 discusses the details of the assessment activities. Table 5-4 presents a schedule of these assessments.

Table 5-4 Assessment Schedule

Agency	Type of Assessment	Agency Assessed	Frequency
NAREL	TSA and PEs, round robin inter-laboratory samples	ERG	Annually

ERG	PEs	Ecology	Annually
OAQPS-EMAD	MSRs, TSAs	ERG, NAREL, EPA Regional and Ecology	As needed by EMAD determination
EPA Region 10	Network Reviews	Ecology	Once every 5 years
EPA Region 10	TSAs and IPAs	Ecology	Annually *

5.5 Schedule of Activities

Table 5-5 contains a list of activities required to plan, implement, and assess the Project.

Table 5-5 Schedule of Activities

Activity	Anticipated Completion Date
Network Development	Complete
Sampler Order	Complete
Personnel Requirements	Ongoing
QAPP Development	12/2000; revised 9/2004
Final Network Design	Complete
Sampler Arrival	Complete
Sampler Siting	Ongoing
Routine Sampling	Ongoing
Sample Analysis	Ongoing
Data Validation	Ongoing
Data Assessment	Ongoing
AQS Submittals	180 days after the Quarter the data was collected in
Final Report	Annually

5.6 Project Records

The Air Quality Program's Quality Assurance Policy and Procedure Manual establishes procedures for the timely preparation, review, approval, issuance, use, control, revision and maintenance of documents and records.

6 Data Quality Objectives

The DQO process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected meets the needs of the intended decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality and quantity needed to meet a program's goals. This process was applied to one of the primary goals of the National Air Toxics Trends Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies. This section describes the results of the DQO process for the local monitoring data requirements for: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde.

In addition, the objectives for other possible future monitoring stations within Washington include:

- Determine and characterize ambient concentrations and depositions of volatile, inorganic and carbonyl air toxic compounds in representative monitoring areas;
- Obtain information on spatial and temporal variability of ambient air toxic compounds;
- Determine air toxic concentrations in areas of high population density;
- Collect data to support and evaluate dispersion and deposition models.

The technical approach used followed the conceptual model developed for the $PM_{2.5}$ FRM DQOs. This conceptual model was followed mainly due to its success in use with $PM_{2.5}$ and the flexibility of the conceptual model. It is a quite general model for simulating the characterization of ambient concentrations in terms of annual or multi-year averages from 1 in 6 day sampling. The model incorporates several sources of variability: seasonal variability, natural day-to-day variability, sampling incompleteness, and measurement error. The measurement error was restricted to a precision component without a bias component because the final mathematical form of the assessment of trends is robust to multiplicative bias. Pollutant specific parameters were used in the modeling. The parameters describing the natural variation of the pollutants were based on data analyses of the EPA's Pilot City data and the Air Toxics Archive. Finally, separate urban and rural DQOs were established for the pollutants that were sufficiently measured in rural locations of the Pilot Study.

A workgroup organized by EPA/OAQPS/EMAD provided representatives of data users, decision makers, state and local parties, and monitoring and laboratory personnel. Battelle provided technical statistical support throughout the process with examples and data analyses. The workgroup guided the DQO development and made the decisions that were not driven by data analyses in the DQO development during a series of conference calls. These decisions included items such as establishing a specific mathematical form for measuring trends and establishing limits on the sampling rate. Battelle and EPA also held a meeting in Research Triangle Park, North Carolina, on June 17, 2002 to discuss the development details.

6.1 The General DQO Process

This section presents an overview of the seven steps in EPA's QA/G-4 DQO process as applied to one of the primary goals of the National Air Toxics Monitoring Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies (see *www.epa.gov/quality/qs-docs/g4-final.pdf*). The purpose of this section is to provide general discussion on the specific issues that were used in developing the DQOs as they relate to the general DQO process.

The DQO process is a seven-step process based on the scientific method to ensure that the data collected meet the needs of its data users and decision makers in terms of the information to be collected, in particular the desired quality and quantity of data. It also provides a framework for checking and evaluating the program goals to make sure they are feasible and that the data are collected efficiently. The seven steps are usually labeled as:

- State the Problem
- Identify the Decision
- Identify the Inputs to the Decision
- Define the Study Boundaries
- Develop a Decision Rule
- Specify Tolerable Limits on the Decision Errors
- Optimize the Design.

6.1.1 The Problem

Characterize the ambient concentrations in the region represented by the monitor to establish any significant downward trend measured by a percent change between successive 3-year means of the concentrations.

The ability to characterize the trends was statistically modeled. The statistical model was designed by starting with a model similar to the one used for $PM_{2.5}$ FRM data. The ambient concentrations are modeled as deviations from a sine curve, where the sine curve represents seasonality. This sine

$$A\left[1+\left(\frac{r-1}{r+1}\right)\sin\left(\frac{day}{365}2\ \pi\right)\right]$$

curve represents long-term daily averages of the concentrations that one would observe at the site. The form used is as follows:

where

A = the long term annual average and
r = the ratio of the highest point on the sine curve to the lowest point. A value of r = 1 indicates no seasonality.

The natural deviations from the sine curve are assumed to follow a lognormal distribution with a mean that is given by the particular point on the sine curve. (For example, the value of the sine curve for Day 100 is the mean for all Day 100s across many years.) The coefficient of variation (CV) of the lognormal distribution is assumed to be a constant. The general model considered also allows for the day-to-day deviations from the sine curve to be correlated, but the current DQOs are based on a correlation of zero. (The correlation effectively measures how quickly the concentrations can change from one deviation from the sine curve to another. A correlation of zero indicates that it can change fast enough that values measured on consecutive days would be completely independent. A value of 0.2 would say that a positive deviation from the curve is somewhat more likely to be followed by another positive deviation than a negative deviation. A value of 0.9 would indicate that positive deviations are almost always followed by another positive deviation.) Finally, the measured values are modeled with a normally distributed random measurement error with a constant coefficient of variation (CV). The specific values for the various parameters are pollutant specific.

The population parameters (the degree of seasonality, the autocorrelation, and the CV of the deviations from the sine curve) were estimated from the Pilot City data (and in the case of benzene compared with estimates from the Air Toxics Data Archive). A near worst-case choice was made for each of the parameters. The power curves and decision errors are established via Monte-Carlo simulation of the model with the particular parameters for various combinations of truth and observed percent changes in three-year mean concentrations. The power curves are plotted as functions of the true percent change in the three-year annual means for compound specific combinations of the sampling frequency, completeness, and precision. Decision errors are stated for these worst-case scenarios.

Note: It was decided by the workgroup from budgetary considerations that the proposed DQOs should be constrained to no more than one in six day sampling.

6.1.2 The Decision

The decision statement provides a link between the principal study question and possible actions. It was decided that any decision would be based on whether or not a 15 percent decrease was observed. Hence the form of the decision was fixed, and may be specified as follows:

Significant decreases (15 percent or more) between successive three-year mean concentration levels will result in …. Insignificant decreases, (increases, or decreases of less than 15 percent) will trigger alternate actions of ….

6.1.3 Identify the Inputs to the Decision

Only six HAPs (benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde) were considered in the DQO development. It is assumed that the other pollutants will be represented by at least one of these six. The statements included here apply implicitly to the other HAPs.

The analytical techniques used in the Pilot study will be used throughout the program. Most importantly for the DQOs the Method Detection Limits (MDLs) will not increase. The pollutant specific MDLs assumed are listed in Section 2 of the Pilot Cities Air Toxics Measurements Summary (http://www.epa.gov/ttn/amtic/files/ambient/airtox/toxics2a.pdf). Those values were identified as pollutant-site maximums that were achieved by at least two of the pilot sites in each pollutant's case.

Among the key decisions made as a part of the DQO process was that each pollutant will need to be measured on a schedule of at least once every six days with a quarterly completeness of 85 percent for six consecutive years. The completeness criterion was checked against the pilot data, and was generally achieved. All valid measurements count toward the completeness goal, including non-detects. The analysis of the trends at the site level will be based on a percent difference between the mean of the first three annual concentrations and the mean of the last three annual concentrations. Hence for each year the annual average concentration, X_i, needs to be found, i = 1, 2, … 6. Next find the mean, X, for the first three years and the mean, Y, for years 4 through 6 as follows:

$$X = \frac{X_1 + X_2 + X_3}{3} \text{ and } Y = \frac{X_4 + X_5 + X_6}{3}.$$

Then the downward trend, T, is the percent decrease from the first three-year period to the second three-year period. Namely,

$$T = \frac{X - Y}{X} \cdot 100.$$

The Action Level is the cutoff point that separates different decision alternatives. Based on the assumed budgetary constraint of one in six day sampling and the natural variation exhibited by the six compounds considered, an action level of 15 percent was chosen. Hence at least a 15 percent decrease between the two distinct three-year mean concentrations will need to be observed in order to be considered a significant decrease. This assumes that the mean concentrations are above the health standards, and hence it makes sense to consider trends. (Note that characterizing the mean concentrations is a separate goal of the Air Toxics program that has not yet been considered and could result in different DQOs.)

6.1.4 The Study Boundaries

While the much of this document is prepared to address the needs of the existing NATTS site located in Seattle at Beacon Hill, it is also intended to cover activities related to toxic monitoring that may occur throughout the state of Washington. The majority of those types of monitoring activities are short duration monitoring projects, usually scheduled for a sampling duration of one year. The Beacon Hill NATTS site is described in detail below.

Beacon Hill (existing site) – This site is in Seattle, an area of high population density that reflects conditions in a "typical" urban residential neighborhood. It is impacted by a mix of urban source categories. It was originally sited to provide neighborhood/urban scale NOx concentrations to compare to the annual NO_2 standard. It is also used to evaluate ozone precursors and the metropolitan area's visibility. The parameters currently measured at this site include VOCs, carbonyls, PM_{10} metals, $PM_{2.5}$ with manual and automated methods, speciated particulate matter with manual and automated methods, carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide, and meteorological conditions. In addition, an Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler, nephelometer and absorption photometer are also being operated at this site.

6.1.5 The Decision Rule

Significant decreases (15 percent or more) between successive three-year mean concentration levels will provide for the identification of successful reduction strategies…. Insignificant decreases, (increases, or decreases of less than 15 percent) will trigger a review of in place reduction measures' effectiveness.

6.1.6 Specify Tolerable Limits on the Decision Errors

Since the program will not generate complete, error-free data, there will be some probability of making a decision error. The main goal of the DQO process is to find a workable balance between how complete and error free the data are with acceptable levels of decision errors. To find the balance, the possible errors need to be carefully defined. This usually needs to be done with the recognition that there will be a range, often called the gray zone, where it is impractical to control decision errors.

The QA/G-4 guidance recommends using 0.01 as the starting point for setting decision error rates. However, such a limit would generally require a sampling rate that is not feasible. The workgroup decided on the following limits:

> *If there is no true decrease in the three-year average concentrations, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.*
>
> *If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is less than 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.*
>
> *Equivalently, the second statement could read that:*
>
> *If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be at least 90 percent.*

The power curves shown in Section 6 show the probability of observing at least a 15 percent decrease as a function of the true decrease. In terms of the above goals this means that the power curve graphs should start below 10 percent for a true percent change of 0 and end above 90 percent for a true percent change of 30 percent. Since there is a particular interest in the error rates for no true change and for a true change of a 30 percent decrease, this associated x-axis (horizontal axis) range is shown for each curve. Also, it is sometimes useful to know when the two target error rates are achieved. The range of “truth” between these values is referred to as the gray zone, i.e., the range of true percent decreases that cannot be reliably detected by the sampling scheme. These are also given for each curve (and indicated with vertical dotted lines).

6.1.7 Optimize the Design

In each pollutant’s case, a sampling schedule of once every six days is set forth with a quarterly completeness criteria of 85 percent. Pilot City study participants were surveyed and almost all were collecting and obtaining valid data values at a rate that exceeded 85 percent for each of the six compounds considered (valid non-detects counted toward completeness). Hence, the target rate of

85 percent was selected, instead of the more common 75 percent completeness goal. This should make the power curves more representative of the network's expected monitoring conditions.

6.1.8 DQO's For the Six Compounds

This section states the design values, namely it gives the expected maximum error rates, gray zones, and power curves for each of the six compounds considered explicitly. The parameters describing the natural state of the ambient conditions used to construct the power curves, error rates and gray zone are compound specific based on data from the Pilot Study. In each case, the Pilot City data yielded a range of estimates. The specific values used were the extremes (or nearly so) that would make detecting a downward trend more difficult. Actual performance in almost all cases should be better than that indicated by the power curves, since specific sites would not be characterized by these extremes in each of these parameters. However, since the sensitivity to the different parameters is not the same, the DQOs need to protect against a combined set of extremes. Hence, the use of extremes for network design purposes is conservative.

Since the rural sites can be quite different from urban sites, separate DQOs are shown in those cases where there were sufficient data to support investigating a separate set of DQOs. In the case of formaldehyde, the urban and rural DQOs are essentially the same.

There are twelve input parameters shown in each section. They are:

1. <u>T1</u>. This is the target error rate for when there is no change. It is always 10 percent.

2. <u>T2</u>. This is the target error rate for when there is a 30 percent decrease. It is always 10 percent.

3. The <u>action limit</u>. This is the minimum observed percent change from the mean concentration of the first three years to the mean concentration from the last three years that would be used to indicate that the concentrations have decreased. Decreases less than this amount would not be considered significant decreases in the mean concentration.

4. The <u>sampling rate</u>. It is set to one in six day sampling in each case.

5. The quarterly <u>completeness</u> criterion. This was set to 85 percent based on the recommendation of ERG and a review of the Pilot Study data completeness.

6. <u>Measurement</u> error Coefficient of Variation (<u>CV</u>). This was assumed to be 15 percent for each compound. (A sensitivity analysis showed that the DQOs are robust to moderate changes in this value.)

7. <u>Seasonality</u> ratio. This is a measure of the degree of seasonality. Specifically, it is the ratio of the highest point on the seasonal curve to the lowest point. A value of 1 indicates no seasonality. Larger values make it more difficult to estimate an annual

or three-year mean concentration, and hence larger values make it more difficult to measure the percent change.

8. Autocorrelation. This is a measurement of how quickly day-to-day deviation from the seasonal curve can occur. A value of 0 indicates that changes occur quickly enough that each day is independent of the preceding day. Values greater than 0 indicate that the changes are generally slower, so that days with concentrations above the seasonal curve are more likely to be followed by another day above the seasonal curve. Values greater than 0 increase the precision of the three-year means and the percent change between the three-year means. Hence, a value of 0 is the most conservative choice for the DQOs. Zero was used in all cases, because many daily measurements are required to obtain a reliable estimate of this parameter.

9. Population CV. This is a measurement of the natural variation about the seasonal curve. Larger values decrease the precision of the three-year mean concentration estimates and the percent change between them. The power curves are strongly dependent on this parameter, but the estimates can be strongly influenced by a few outlier values. Generally the 90th percentile of the estimates from the Pilot study was used as a balance between these competing forces. This value was then rounded up to be a multiple of 5 percent for the urban DQOs. For the rural DQOs an additional 5 percent was added, since there were fewer rural sites on which to base the estimates.

10. MDL. This is the MDL used in the simulations. The value was chosen to be a reasonably attainable maximum for a site and compound.

11. Initial mean concentration. This is the mean concentration of the first three years in the simulations. Values closer to the MDL decrease the precision of the percent change estimate. The value chosen was approximately equal to the 25th percentile of the site-compound means from the Pilot study.

12. Health Risk Standard. This value is shown for reference only. It was not used in the simulations.

In addition to the power curves, there are three sets of output values.

1. $Error_0$ is the percent of the simulations with no change in the true three-year means that in fact generated at least a 15 percent decrease in the observed three-year means.

2. $Error_{30}$ is the percent of the simulations with a 30 percent decrease in the true three-year means that generated less than a 15 percent decrease in the observed three-year means.

3. The gray zone is the interval of the true decreases that cannot be detected with confidence by the study design. In this range, the probability of observing at least a 15 percent decrease is greater than 10 percent, but less than 90 percent.

In summary, based on variability and uncertainty estimates from the ten-city Pilot Study, the following Sections 3.1 through 3.10 suggest that the specified air toxics trends DQOs will be met for monitoring sites that satisfy the goals of 1 in 6 day sampling, 85 percent completeness, and 15 percent measurement CV. These results were explicitly developed for benzene (urban and rural); 1,3-butadiene (urban and rural); arsenic (urban and rural); chromium (urban only); acrolein (urban only); and formaldehyde (urban and rural).

6.1.9 DQO's for Measuring the Percent Decrease

6.1.9.1 Benzene at Urban Locations

Table 6.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at urban locations. Table 6.2 shows the output values from the simulations. Figure 6.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.2 suggests that the specified air toxics trends DQOs will be met for benzene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.1 DQO input parameters for benzene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (μg/m^3)
10%	15%	1 in 6 day	4.5	85%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.044	0.128

Table 6.2 DQO output parameters for benzene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
6%	97%	3% - 26%

Figure 6.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in urban locations of the Pilot Study

6.1.9.2 DQOs for Measuring the Percent Decrease of Benzene at Rural Locations

Table 6.3 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at rural locations. Table 6.4 shows the output values from the simulations. Figure 6.2 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.4 suggests that the specified air toxics trends DQOs will be met for benzene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.3 DQO input parameters for benzene at rural locations

T1	**Action Limit**	**Sampling Rate**	**Seasonality**	**Population CV**	**Initial Concentration (μg/m^3)**
10%	15%	1 in 6 day	4.0	60%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.044	0.128

Table 6.4 DQO output parameters for benzene at rural locations

Error rate for no true change	**Error rate for 30% decrease**	**Gray zone**
2%	99%	7% - 23%

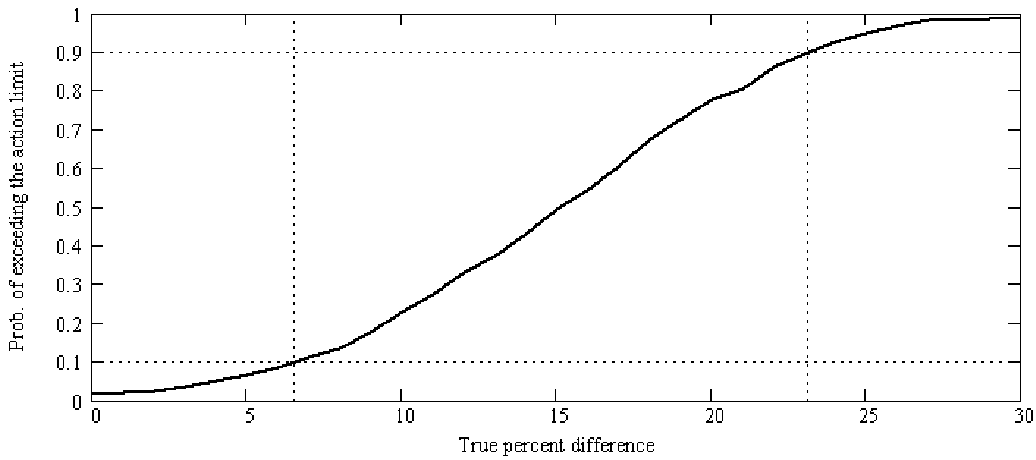


Figure 6.2 **Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in rural locations of the Pilot Study**

6.1.9.3 DQOs for Measuring the Percent Decrease of 1,3-Butadiene at Urban Locations

Table 6.5 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at urban locations. Table 6.6 shows the output values from the simulations. Figure 6.3 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.6 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.5 DQO input parameters for 1,3-butadiene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (μg/m^3)
10%	15%	1 in 6 day	7.0	100%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.02	10^{-5}

Table 6.6 DQO output parameters for 1,3-butadiene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
10%	94%	0% - 28%

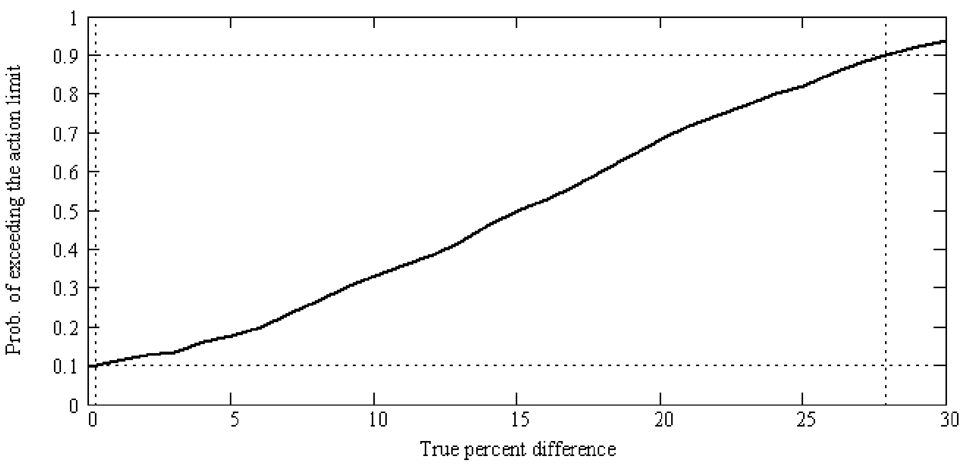


Figure 6.3 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in urban locations of the Pilot Study

6.1.9.4 DQOs for Measuring the Percent Decrease of 1,3-butadiene at Rural Locations

Table 6.7 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at rural locations. Table 6.8 shows the output values from the simulations. Figure 6.4 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.8 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.7 DQO input parameters for 1,3-butadiene at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (μg/m^3)
10%	15%	1 in 6 day	6.0	75%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.02	10^{-5}

Table 6.8 DQO output parameters for 1,3-butadiene at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
4%	98%	4% - 25%

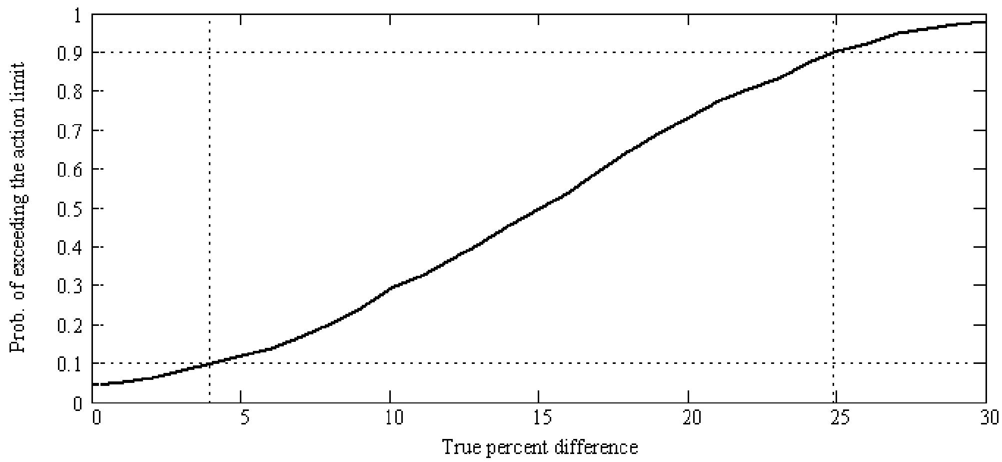


Figure 6.4 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in rural locations of the Pilot Study

6.1.9.5 DQOs for Measuring the Percent Decrease of Arsenic at Urban Locations

Table 6.9 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at urban locations. Table 6.10 shows the output values from the simulations. Figure 6.5. shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.10 suggests that the specified air toxics trends DQOs will be met for arsenic at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.9 DQO input parameters for arsenic at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (μg/m^3)
10%	15%	1 in 6 day	5.0	85%	0.002

T2	Measurement CV	Completeness	Autocorrelation	MDL ($\mu g/m^3$)	Risk Standard ($\mu g/m^3$)
10%	15%	85%	0	0.000046	0.0043

Table 6.10 DQO output parameters for arsenic at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	95%	2% - 27%

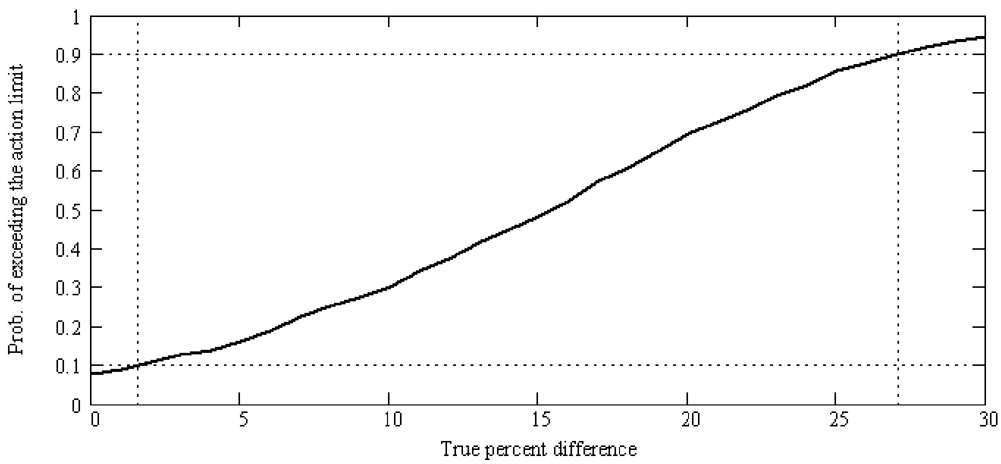


Figure 6.5 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in urban locations of the Pilot Study

6.1.9.6 DQOs for Measuring the Percent Decrease of Arsenic at Rural Locations

Table 6.11 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at rural locations. Table 6.12 shows the output values from the simulations. Figure 3.6.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.12 suggests that the specified air toxics trends DQOs will be met for arsenic at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.11 DQO input parameters for arsenic at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.0	65%	0.001
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.000046	0.0043

Table 6.12 DQO output parameters for arsenic at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
3%	99%	5% - 24%

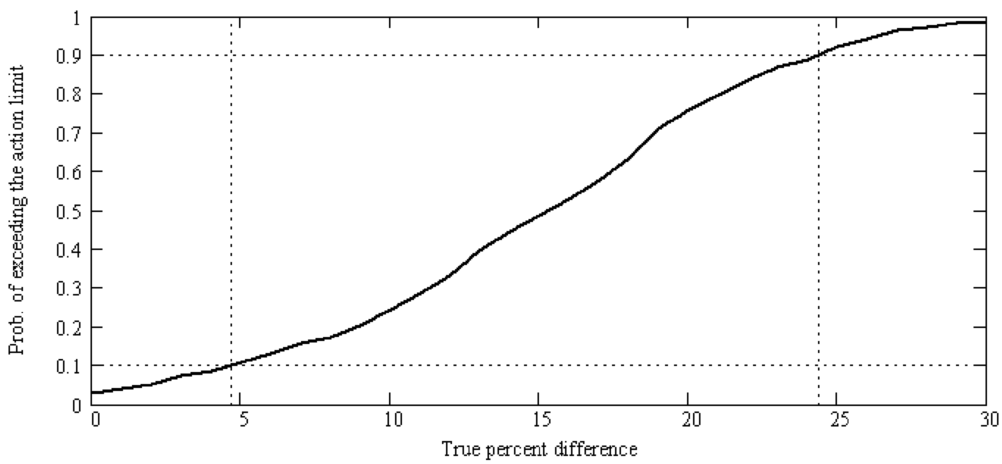


Figure 6.6 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in rural locations of the Pilot Study

6.1.9.7 DQOs for Measuring the Percent Decrease of Chromium

Table 6.13 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of chromium. Table 6.14 shows the output values from the simulations. Figure 6.7 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.14 suggests that the specified air toxics trends DQOs will be met for chromium at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 6.13 DQO input parameters for chromium

T1	**Action Limit**	**Sampling Rate**	**Seasonality**	**Population CV**	**Initial Concentration (μg/m^3)**
10%	15%	1 in 6 day	5.0	90%	0.0015
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.00018	0.012

Table 6.14 DQO output parameters for chromium

Error rate for no true change	Error rate for 30% decrease	Gray zone
7%	96%	2% - 27%

Figure 6.7 Power curve for detecting a 15 percent decrease between successive three-year means of chromium concentrations based on the data variation found in of the Pilot Study

6.1.9.8 DQOs for Measuring the Percent Decrease of Acrolein

Table 6.15 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of acrolein. Table 6.16 shows the output values from the simulations. Figure 6.8 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.16 suggests that the specified air toxics trends DQOs will be met for acrolein at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.15 DQO input parameters for acrolein

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration (μg/m^3)
10%	15%	1 in 6 day	4.0	105%	0.4
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.14	-

Table 6.16 DQO output parameters for acrolein

Error rate for no true change	Error rate for 30% decrease	Gray zone

10%	91%	0% - 29%

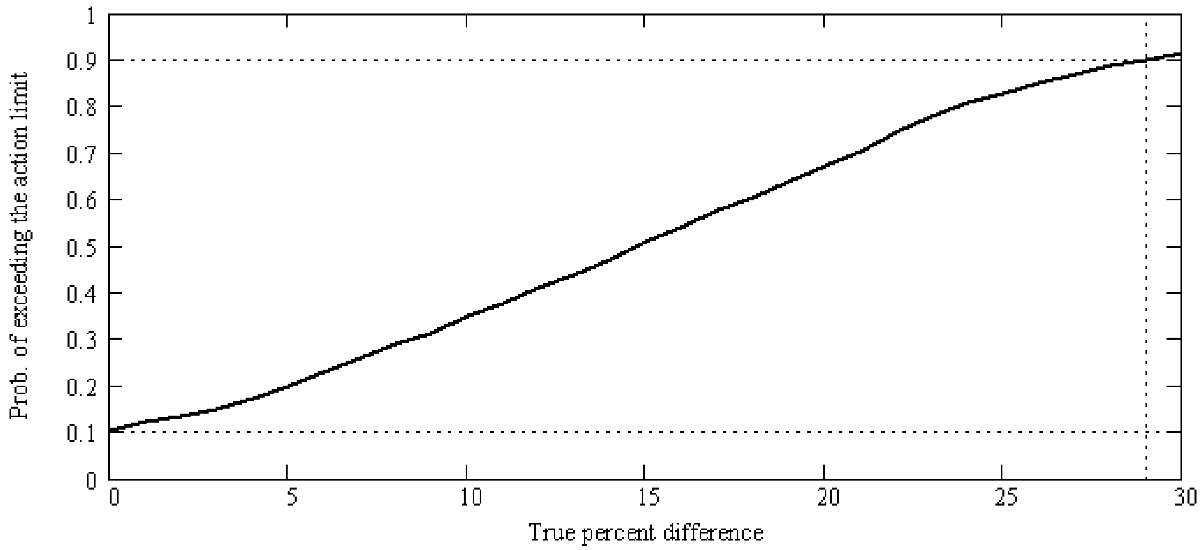


Figure 6.8 Power curve for detecting a 15 percent decrease between successive three-year means of acrolein concentrations based on the data variation found in the Pilot Study

6.1.9.9 DQOs for Measuring the Percent Decrease of Formaldehyde at Urban Locations

Table 6.17 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at urban locations. Table 6.18 shows the output values from the simulations. Figure 6.9 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.18 suggests that the specified air toxics trends DQOs will be met for formaldehyde at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV.

Table 6.17 DQO input parameters for formaldehyde at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	90%	2.5
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.014	$1.3\ 10^{-5}$

Table 6.18 DQO output parameters for formaldehyde at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	95%	2% - 27%

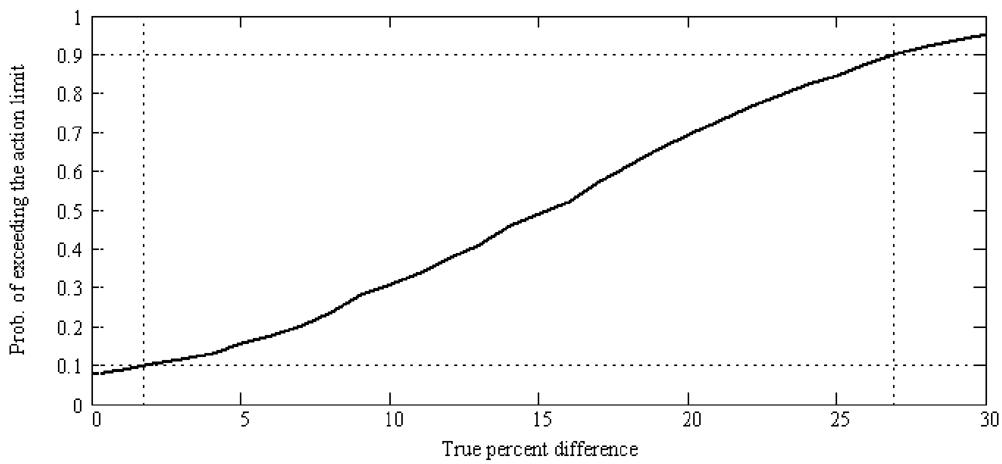


Figure 6.9 Power curve for detecting a 15 percent decrease between successive three-year means of formaldehyde concentrations based on the data variation found in urban locations of the Pilot Study

6.1.9.10 DQOs for Measuring the Percent Decrease of Formaldehyde at Rural Locations

Table 6.19 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at rural locations. Table 6.20 shows the output values from the simulations. Figure 6.10 shows the associated power curve, which is the probability of observing a 15percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 6.20 suggests that the specified air toxics trends DQOs will be met for formaldehyde at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15percent measurement CV.

Table 6.19 DQO input parameters for formaldehyde at rural locations

T1	**Action Limit**	**Sampling Rate**	**Seasonality**	**Population CV**	**Initial Concentration (μg/m^3)**
10%	15%	1 in 6 day	7.0	90%	2.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL (μg/m^3)**	**Risk Standard (μg/m^3)**
10%	15%	85%	0	0.014	1.3 10^{-5}

Table 6.20 DQO output parameters for formaldehyde at rural locations

Error rate for no true change	**Error rate for 30% decrease**	**Gray zone**
8%	95%	1% - 27%

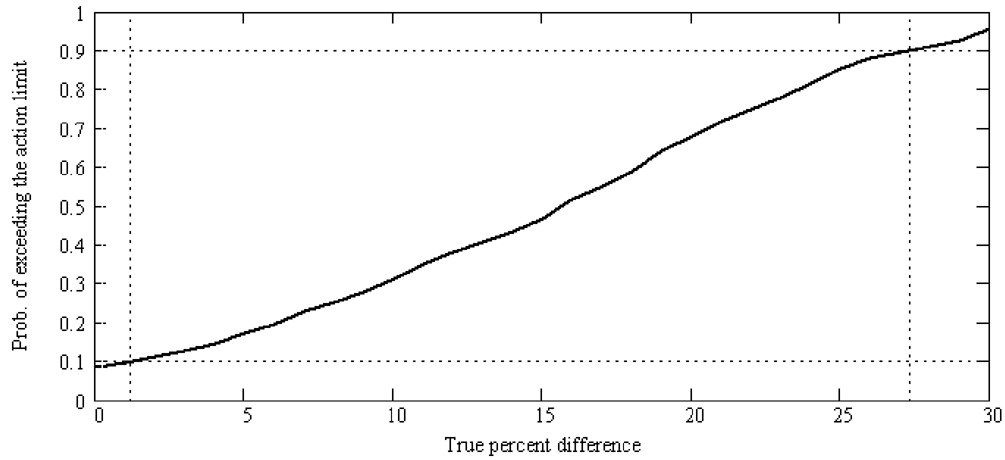


Figure 6.10 Power curve for detecting a 15 percent decrease between successive three-year means of formaldehyde concentrations based on the data variation found in rural locations of the Pilot Study

7 Training

Air monitoring personnel will be recruited and screened to ensure they are experienced and qualified.

Air monitoring personnel will receive sufficient training in their appointed jobs to contribute to the reporting of complete and high quality data. Workshops and courses will be provided by EPA. Primary responsibility for training will rest with the individual's supervisor.

Prior to installation of new equipment, station operators will attend training sessions where either experienced air monitoring field staff or Air Monitoring Unit personnel will familiarize them with the operation, calibration and maintenance of the new equipment.

8 Documentation and Records

The Air Quality Program's Quality Assurance Policy and Procedure Manual describes document and records procedures. WSU will provide quarterly reports to the Ecology Air Toxics Monitoring Coordinator (John Williamson). The reports will provide concentration data for the toxic species for reporting to AQS. Annually WSU will compile all of the data into a final summary report for use by Ecology. The quarterly and annual reports will be in the form of electronic and hardcopy submissions. Data will also be posted and available on the Ecology's web page located at https://fortress.wa.gov/ecy/aqp/Toxics/AnnualToxicsSummaries.shtml

At a future date, it is expected that technical publications and graduate student theses will be derived from this work.

The Air Quality Program Manager will certify that the annual summary is accurate to the best of his/her knowledge. This certification will be based on the various assessments and reports performed by the organization.

9 Sampling Design

9.1 Scheduled Project Activities, Including Measurement Activities

Ecology is currently monitoring concentrations at one location, the Seattle Beacon Hill NATTS site; however this section will apply to future sites designed and operated for short duration studies. Therefore, this section will discuss the operation and installation of samplers at the NATTS. Since the NATTS is a nationally recognized monitoring location each system (with the exception of the Aethalometer), will be collocated. Since Ecology participated in the National Air Toxics Pilot Program, many of the samplers were already in place.

9.2 Rationale for the Design

9.2.1 Primary Samplers

The purpose of the NATTS site is to determine the long term trends. By employing samplers that are described in the appropriate compendia[1,2,3], the data collected will be comparable to standard EPA methods. By complying with the sampling frequency requirements of *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*[4], Ecology assumes that the sampling frequency is sufficient to attain the desired confidence in the annual 95th percentile and annual mean of concentrations. By selecting locations using the rules in *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*, Ecology can be confident that the concentrations within its jurisdiction are adequately characterized. Sampler type, frequency, and siting are further described in section 9.4.

9.2.2 QA Samplers

The purpose of collocated samplers and the performance evaluation is to estimate the precision of the various systems samplers. The goal of is to have concentrations measured by a sampler be within ±10% of the true concentration and that the precision have a coefficient of variation less than 10%. To estimate the level of precision being achieved in the field, the NATTS site will operate collocated samplers for VOC and PM_{10} metals. The Aldehyde samplers have a dual channel configuration, which allows DNPH cartridges to be loaded and allowed to collect samples on the same instrument as the primary sample. The QA samples will be set, run and collected on a 1 in 12 day schedule. There will be 2 analytes from each instrument that will be used to determine the precision.

Field accuracy will be estimated using flow, temperature sensor and barometric checks. Laboratory accuracy will be determined by the analysis of known reference analytes prepared by independent laboratories submitted to the WSU laboratory when available through EPA. If a sampler and laboratory equipment are operating within the required precision and accuracy levels, then the decision maker can proceed knowing that the decisions will be supported by unambiguous data. Thus the key characteristics being measured with the QA samplers are precision.

9.3 Design Assumptions

The sampling design is based on the assumption that following the rules and guidance provided in CFR and *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants* will result in data that can be used to measure compliance with the national standards. The only issue at Ecology's discretion is the sampler siting, and to a degree, sampling frequency. The siting assumes homogeneity of concentrations within the MSA. Boundaries will be regularly reviewed, as part of the network reviews. The basis for creating and revising the boundaries is described in the following section.

9.4 Procedure for Locating and Selecting Environmental Samples

9.4.1 Sampling Design

The design of the air toxics network must achieve the monitoring objective. For the Seattle Beacon Hill NATTS site, the objectives are stated in Statement 1 and for any future short term monitoring sites, the objective is stated in Statement 2.

Detect a percent difference change between successive three-year average concentration levels that are greater than or equal to 15 percent

Determine the highest concentrations expected to occur in the area covered by the network, i.e., to verify the spatial and temporal characteristics of HAPs within the city.

The procedure for siting the samplers to achieve the objective is based on judgmental sampling, as is the case for most ambient air monitoring networks. Judgmental sampling uses data from existing monitoring networks, knowledge of source emissions and population distribution, and inference from analyses of meteorology to select optimal sampler locations. The exact location is discussed in Section 9.4.2.

9.4.2 Sampling Locations

Beacon Hill (NATTS site) – This site is in an area of high population density that reflects conditions in a "typical" urban residential neighborhood. It is impacted by a mix of urban source categories. It was originally sited to provide maximum neighborhood/urban scale NOx concentrations to compare to the annual NO_2 standard. It is also used to evaluate ozone precursors and the metropolitan area's visibility. The parameters currently measured at this site include VOCs, carbonyls, PM_{10} metals, $PM_{2.5}$, speciated particulate matter, carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide, sulfates, nitrates, EC/OC, and meteorological conditions. In addition, an Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler and nephelometer are also being operated at this site. An IMPROVE sampler was operated at this site from March 1996 through September 1999 for the purpose of evaluating regional haze, urban visibility and source apportionment.

Figure 9-1 Seattle Beacon Hill NATTS Location

Figure 9-2 Seattle Beacon Hill NATTS Location Aerial Photo

9.5 Classification of Measurements as Critical/Noncritical

The ambient concentration and site location data is identified in AQS. The information collected at collocated samplers is the same as that presented in Tables 5-1, 5-2, 5-3 and 5-4 for primary samplers. All of the measurements in these tables are considered critical because it forms the basis for estimating precision, which are critical for evaluating the ability of the decision makers to make decisions at desired levels of confidence.

9.6 Validation of Any Non-Standard Measurements

At this time there are no NAAQS for the air toxics compounds, with the except for lead. Ecology deploys and operates instruments according to descriptions in the applicable EPA guidance documents.

References

1. Compendium Method for the Determination of Inorganic Compounds in Air, United States Environmental Protection Agency, June 1999, Section IO-2.1.

2. Compendium Method for the Determination of Toxic Organic Compounds in Air, United States Environmental Protection Agency, Section TO-11A, January 1999

3. Compendium Method for the Determination of Toxic Organic Communes in Air, United States Environmental Protection Agency, Section TO-15, January 1999

4. Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants, EPA Document Number, EPA 450/4-84-022, September 1984.

10 Sampling Methods

The following sampling methods will be utilized in determining the pollutants listed in Section 4.2: EPA methods IO-3.5 (ICP-MS) for metals, TO-15 for VOCs, and TO-11A for Carbonyls.

10.1 Sample Collection and Preparation

The sampling frequency for VOCs and Carbonyls are once every six days while the Aethalometer is a continuous instrument. The sampling schedule is consistent with the one-in-six timing relative to the EPA's published Monitoring Schedule. All samples are 24-hr integrated samples. This will yield about 60 sampling days at each site per year for determination of the toxic compounds designated program. In addition, there will be about 30 collocated sampling days. All samples will be shipped from the Ecology NWRO to WSU-LAR within three days following collection.

Sample medium preparation involves weighing PM_{10} filters and cleaning canisters. One randomly selected canister in each cleaned batch is analyzed for the target compounds. If the concentration of any of the target compounds exceeds the MDL for that species, the entire batch must be re-cleaned and undergo a new certification test.

PM_{10} filter receipt, inspection, numbering, conditioning and storage are described in Section 5.3.

VOC clean up, certification and storage are described in Section 5.3.

Carbonyl cartridge certification and handling are described in Section 5.3.

10.2 Sample Set-up

Air monitoring station operators are responsible for sample collection set-up and collection. The Air Monitoring Unit will provide the appropriate equipment and technical assistance to the air monitoring station operators with the installation. The frequency of sample collection is described in Section 5.1 and will follow the published Monitoring Schedule. Air monitoring station operators will use the following Standard Operating Procedures prepared by Ecology:

- Carbonyl Compounds Air Sampling Procedures
- Volatile Organic Compound Sampling Procedure
- Aethalometer Operating Procedure
- High Volume PM_{10} Volumetric Flow Controlled Procedure

Representativeness will be achieved by adhering to the specifications in 40 CFR 58, Appendix D, "Network Design for State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS)" and Appendix E, "Probe Siting Criteria for Ambient Air Quality Monitoring".

10.3 Sampling Measurement System Corrective Actions

Corrective action measures will be taken to ensure data quality objectives are attained and are described in the Table 10.3 below.

Table 10.3

Item	Problem	Action	Responsible Party
Pre/Post Filter Inspection	Pinholes/Tears Visual detection of a leak	Void Sample Document in log book; notify field operator	Laboratory
Erratic Flow Rates	Motor near failure	Document in log book; notify lab; flag data	Field operator; Laboratory
PM_{10} Sample Flow Rate $>\pm$ 10%	Leak in sampling train/out of calibration	Document in log book; notify lab; recalibrate; flag data	Field operator; Laboratory
Leak Test	Canister won't hold pressure	Document in log book; inspect connections; flag data	Field operator; Laboratory
Carbonyl Sample Flow Rate $>\pm$ 10%	Leak in sampling train/out of calibration	Document in log book; notify lab; recalibrate; flag data	Field operator; Laboratory

Elapsed Time >± 10 min/day	Check programming; verify if power outage	Document in log book; notify lab; reprogram; flag data	Field operator; Laboratory
Elapsed Time; sample didn't run	Check programming	Document in log book; notify lab; reprogram	Field operator

10.4 Sampling Equipment, Preservation, and Holding Time Requirements

For data comparability, the National Air Toxics program specifies the EPA methods: IO-3.5 (ICP-MS) for metals, TO-15 for VOCs, and TO-11A for Carbonyls which are used for sampling each suite of the air toxic parameters. The sample medium storage temperature, temperature and chemical preservation, holding time and air sample volume requirements are specified in each of these methods.

10.5 Sample Contamination Prevention

The Air Monitoring network has rigid requirements for preventing sample contamination. These requirements are discussed in the Air Quality Program's Quality Assurance Policy and Procedure Manual.

11 Sample Custody

Figure 11.1 and 11.2 below represents the chain of custody form used to track the carbonyl tubes and canisters. The chain of custody form in Ecology's "High Volume PM_{10} Volumetric Flow Controlled Procedure" will be used to track the PM_{10} filters.

Figure 11.1
Carbonyl Field Data Sheet

A. General Information

Site Location____

Sample Setup Date ____/_____/____ Time ______PST_ Operator ____________________

Sample Recovery Date ____/_____/____ Time _______PST Operator ____________________

B. Sampling Information

Sample Cartridge ID: _____________________________ Sampler ID:___________________________

Duplicate Cartridge ID: _____________________________

Field Blank: □Yes □ No Field Blank ID Number_______________________

Start Date: _____/_____/_____@_________PST End Date: _____/_____/_____@________PST

Indicated Flow Rate: __________________cc/min Indicated Sample Volume: ______________liters

Duration:____________________________hr:min

C. Laboratory Information

Analysis Date: _____/_____/_____ Analysis Time : ___________________PST_

Date Received :_____/_____/_____ Data File Name :_______________________

Laboratory Technician: ____

D. Comments:

A single instrument is used to collect the sample (Channel A), duplicate (Channel B) and field blank. Flow rates, sampled volumes and duration are common to both the sample and duplicate. There is no flow through the blank.

Figure 11.2
VOC Field Data Sheet

A. General Information

Site
Location____

Sample Setup Date ____/____/____ Time_______PST Operator: __________

Sample Recovery Date ____/____/____ Time_______PST Operator: ___________

B. Sample Information

Sample Canister ID: ________________ Sampler Instrument ID:________________.__

Canister Pressure at Setup __________ Canister Pressure at Recovery ______________psi

Start____/____/____@____________PST End____/____/____@______________PST
Indicated Flow Rate:_______cc/min Indicated Sample Volume:_________________liters
Sample Duration: ___________________hr:min

C. Duplicate Information

Sample Canister ID: __________________ Sampler Instrument ID:___________________

Canister Pressure at Setup _____________ Canister Pressure at Recovery ____________psi

Start_____/_____/_____@___________PST End_____/_____/_____@______________PST
Indicated Flow Rate:_____________cc/min Indicated Sample Volume:_______________liters
Sample Duration: ___________________hr:min

D. Laboratory Information

Date Received ____/____/____ Analysis Date ____/____/____ Analysis Time _______ PST

Final Canister Pressure: _________ FID File Name:_________ ECD File Name:__________

Laboratory Technician:____

COMMENTS:

12 Analytical Methods

Analytical methods that are used for the analysis of each suite of air toxics parameters are as follows. Ambient air samples will be collected at a frequency of 1 every six days. Air samples collected in certified clean canisters are analyzed for the core HAP Volatile Organic Compounds (VOCs) using the Compendium Method TO-15. Air samples collected in DNPH-coated cartridges are analyzed for carbonyl compounds using the Compendium Method TO-11A (HPLC). The VOC and carbonyl analyses are performed by Washington State University (Laboratory for Atmospheric Research). PM_{10} filter samples collected are analyzed for metals (cadmium, chromium, lead, beryllium, nickel, manganese and arsenic (optional)) using the Compendium Method IO-3.5 (ICP/MS). The metals analyses are performed by Energy Northwest Environmental Services Laboratory. Collocated samples are analyzed for VOCs, carbonyls and metals following the same methods stated above. All of the QA/QC requirements of the methods specified above shall be followed throughout the sample collection and analysis process of this program

13 Quality Control Requirements

The quality control procedures specified in 40 CFR 58, Appendix A and EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volumes II and IV will be utilized to check the quality of the data. Quality control activities, including precision checks, will be documented on the chart and station logbook. The quality control checks for the analytical instrumentation will be performed in accordance with EPA's "Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program". The frequencies, control limits, and corrective actions associated with the field equipment are presented in Table 13.

Table 13 - Quality Control Checks

Parameter	Check	Control Limit	Corrective Action
Manual Method	**Monthly**		
PM_{10} and	Flow Check	> ±7%	Re-calibrate
Continuous		> ±10%	Rectify Problem, Flag Data
Aethalometer			
VOC (Xontech)	**Monthly**		
	Leak Check	Leak indicated	Rectify Problem, Flag Data
Carbonyl	**Quarterly**		
(Xontech)	Flow/Leak Check	> ±10%	Rectify Problem, Flag Data
Carbonyl	**Monthly**		
(Xontech)	Leak Check	Leak indicated	Rectify Problem, Flag Data
Meteorological	**Quarterly**		
	Wind Speed	> ±5%	Invalidate Data
	Wind Direction	> ±3°	Rectify Problem
		> ±5°	Invalidate Data
	Temperature	> ±0.5°	Invalidate Data

14 Procurement, Acceptance Testing, and Maintenance Requirements for Instruments, Supplies and Consumables

This section details the procedures used for procuring, inspecting, testing, and accepting instruments, supplies and consumables that directly or indirectly affect data quality. The sampling and analytical methods (TO-15, TO-11A & IO-3.5) clearly specify the instruments, supplies, and consumables that will be employed in this program. Each laboratory has developed Standard Operating Procedures (SOPs) for maximizing data quality.

14.1 Procurement and Acceptance Testing of Equipment

The Air Monitoring Coordinator is responsible for identifying air monitoring equipment needs and approving equipment purchases. The following protocol is used in procurement of air monitoring equipment:

- Equipment evaluation and selection. Prior to purchase, the equipment's performance will be evaluated and other users queried in regard to the performance, dependability and ease of operation.
- Purchase specifications. The purchase contract will state the performance specifications that insure only equipment of the desired quality is obtained, require a one year warranty, and indicate payment will not be made until the equipment has passed an acceptance test.
- Acceptance Testing. Prior to payment, the equipment will be tested to ensure that it meets the requirements listed in the purchase specifications. For analyzers, the minimum test consists of checking zero drift, span drift, voltage stability, temperature stability, and linearity.

14.2 Maintenance of Equipment

Utilizing the specifications in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II and IV and specific instrument manufacturer's manuals, preventive and remedial maintenance tasks, schedules, parts and supplies will be maintained by the Air Monitoring Unit.

The Station Operators are responsible for performing routine preventive and corrective maintenance. They will prepare maintenance reports that will be reviewed and archived by the Air Monitoring Unit.

Major maintenance and repair will be performed by the by the Air Monitoring Unit. For each criteria pollutant, specific frequency requirements and schedules are specified in the Air Quality Program's Quality Assurance Policy and Procedure Manual.

15 Instrument Calibration and Frequency

Instrumentation specific to the laboratory are calibrated as often as specified in methods TO-15, TO-11A, & IO-3.5 and in accordance with the requirements set forth by the analytical methods. Instruments and equipment used in the field will be calibrated at the required frequency stated in the SOPs or in accordance with the manufacturer's specifications.

16 Data Acquisition Requirements

This section addresses data not obtained by direct measurement from the Air Quality Program. This includes both outside data and historical monitoring data. Non-monitoring data and historical monitoring data are used by the Program in a variety of ways. Data obtained in this manner must comply with the requirements for data acceptance as outlined in the Air Quality Program's Quality Assurance Policy and Procedure Manual.

17 Data Management

This section addresses data management procedures used in support of the Air Quality Program. Specific details of data recording, processing, validation, assessment, transmittal, reporting, archiving and retrieval are discussed in the Air Quality Program's Quality Assurance Policy and Procedure Manua*l* and in the following sections.

17.1 Data Recording

Air monitoring station reports (Site Masters) will be prepared by the Station Operators and revised when changes in the instrumentation or surrounding area occur. These reports will identify the station name, station number, date, time, operator, instrument identification, parameter, scale and units. Additionally, the report will document the station location, address, UTM coordinates, elevation, and probe location. These reports will be sent to the Air Monitoring Unit for review, processing and archiving.

Air monitoring equipment calibration reports will be prepared and archived by the Air Monitoring Unit.

The Station Operators will maintain station logbooks documenting operational and maintenance activities at the monitoring site. The logbook will be identified with the station name, station number, date, time, operator, instrument identification, parameter, scale and units. The log book will be used to document quality control checks (time, zero, span, precision, calibration, temperature, pressure, flow, etc.), maintenance, audits, equipment changes (span gas, permeation tubes, analyzer, recorder, pen, paper, probe, etc), and missing or invalid data. The logbooks will be reviewed by the Quality Assurance Unit and archived by the Air Monitoring Unit.

17.2 Data Processing and Reporting

Data from all of the laboratory analyses are collected, processed and stored by computers associated with the individual instruments. Electronic files from the instrumental data systems are typically transferred to Excel Spreadsheets for tabulation and report preparation. WSU will compile all of the analytical data and provide QA and ambient data reports to Ecology on a quarterly basis. An annual report will be prepared following the 12-month sampling period. WSU graduate students may use the data generated in this program as theses material. In addition, WSU, Energy Northwest, and Ecology scientists will co-author technical publications using the data gathered in this program.

17.3 Data Transmittal

Data transmittal occurs when data are transferred from one person or location to another or when data are copied from one form to another. Air quality data and information will be fully screened and validated and will be submitted directly to the AQS via electronic transmission, in the format of the AQS, and in accordance with the quarterly schedule defined in Table 5.5.

17.4 Data Reduction

Data reduction processes involve aggregating and summarizing results so that they can be understood and interpreted in different ways. The ambient air monitoring regulations require certain summary data to be computed and reported regularly to U.S. EPA. Other data are reduced and reported for other purposes such as station maintenance.

18 Assessments and Response Actions

An assessment, for this Plan, is defined as an evaluation process used to measure the performance or effectiveness of the quality system, the establishment of the monitoring network and sites and various measurement phases of the data operation.

18.1 Assessment Activities and Project Planning

18.1.1 Management Systems Review (MSR)

An MSR is a qualitative assessment of a data collection operation or organization to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate. MSRs will be conducted every three years by EPA. The MSR will use appropriate regulations, and the QAPP to determine the adequate operation of the program and its related quality system. The quality assurance activities of all criteria pollutants including air toxics will be part of the MSR. EPA staff will report its findings within 30 days of completion of the MSR. The report will be appropriately filed. Follow-up and progress on corrective action(s) will be determined during regularly scheduled division directors meetings.

18.1.2 Network Reviews

Conformance with network requirements of the monitoring network is accomplished through annual reviews. The network review is used to determine how well a particular air monitoring network is achieving its required air monitoring objective, and how it should be modified to continue to meet its objective. Since the NATTS site will be collecting long term trends data and is not anticipated to move, the network review will not be performed. Other short term monitoring sites will be expected to collect data for only one year and therefore a network review will not be needed it that case either.

18.1.3 Technical Systems Audits (TSA)

A TSA is a thorough and systematic on-site qualitative audit, where facilities, equipment, personnel, training, procedures, and record keeping are examined for conformance to the QAPP. TSAs of the network will be accomplished every three years and will be conducted by the EPA Regional Office. EPA will implement the TSA either as a team or as an individual auditor. EPA will perform TSA activities that that will focus on:

- Field - handling, sampling, shipping.;
- Laboratory - Pre-sampling, shipping, receiving, post-sampling weighing, analysis,

archiving, and associated QA/QC;
- Data management - Information collection, flagging, data editing, security, upload.

Key personnel to be interviewed during the audit are those individuals with responsibilities for: planning, field operations, laboratory operations, QA/QC, data management, and reporting. To increase uniformity of the TSA, an audit checklist will be developed and used. This checklist is based on the *EPA R-5* guidance.

The audit team will prepare a brief written summary of findings, organized into the following areas: planning, field operations, laboratory operations, quality assurance/quality control, data management, and reporting. Problems with specific areas will be discussed and an attempt made to rank them in order of their potential impact on data quality.

The audit finding form has been designed such that one is filled out for each major deficiency that requires formal corrective action. The finding should include items like: systems impacted, estimated time period of deficiency, site(s) affected, and reason of action. The finding form will inform Ecology about serious problems that may compromise the quality of the data and therefore require specific corrective actions. They are initiated by the Audit Team, and discussed at the debriefing

Post-Audit Activities- The major post-audit activity is the preparation of the systems audit report. The report will include:

- Audit title and number and any other identifying information;
- Audit team leaders, audit team participants and audited participants;
- Background information about the project, purpose of the audit, dates of the audit; particular measurement phase or parameters that were audited, and a brief description of the audit process;
- Summary and conclusions of the audit and corrective action requires;
- Attachments or appendices that include all audit evaluations and audit finding forms.

To prepare the report, the audit team will meet and compare observations with collected documents and results of interviews and discussions with key personnel. Expected QA Project Plan implementation is compared with observed accomplishments and deficiencies and the audit findings are reviewed in detail. Within thirty (30) calendar days of the completion of the audit, the audit report will be prepared and submitted. The systems audit report will be submitted to the appropriate managers and appropriately filed.

If the Ecology has written comments or questions concerning the audit report, the Audit Team will review and incorporate them as appropriate, and subsequently prepare and resubmit a report in final form within thirty (30) days of receipt of the written comments. The report will include an agreed-upon schedule for corrective action implementation.

Follow-up and Corrective Action Requirements- EPA and Ecology will work together to solve required corrective actions. As part of corrective action and follow-up, an audit finding response letter will be generated by Ecology. The audit finding response letter will address what actions are being implemented to correct the finding of the TSA. The audit response letter will be completed within 30 days of acceptance of the audit report.

18.1.4 Performance Audit

A Performance Audit is a field operations audit that ascertains whether the samplers are operating within the specified limits as stated in the SOPs and QAPP. The Performance Audit will be performed by Ecology at least once every year. The audit consists of challenging the samplers to operate using independent NIST-traceable orifices or other flow devices. Once the audit has been performed, the flow rate is calculated and compared against the flow rates as specified in the QAPP or SOPs. If the flow rates are not within these ranges, then the field operations technician is notified in writing and corrective action ensues. Once the field technicians have remedied the situation, a post audit confirms the adjustment or maintenance.

18.1.5 Data Quality Assessments

A data quality assessment (DQA) is the statistical analysis of environmental data to determine whether the quality of data is adequate to support the decision which are based on the DQOs. Data are appropriate if the level of uncertainty in a decision based on the data is acceptable. The DQA process is described in detail in *Guidance for the Data Quality Assessment Process*, EPA QA/G-9 and is summarized below.

- *Review the data quality objectives (DQOs) and sampling design of the program*: review the DQO. Define statistical hypothesis, tolerance limits, and/or confidence intervals.

- *Conduct preliminary data review*. Review Precision &Accuracy (P&A) and other available QA reports, calculate summary statistics, plots and graphs. Look for patterns, relationships, or anomalies.

- *Select the statistical test*: select the best test for analysis based on the preliminary review, and identify underlying assumptions about the data for that test.

- *Verify test assumptions*: decide whether the underlying assumptions made by the selected test hold true for the data and the consequences.

- *Perform the statistical test:* perform test and document inferences. Evaluate the performance for future use.

Measurement uncertainty will be estimated for both automated and manual methods. Terminologies associated with measurement uncertainty are found within 40 CFR Part 58 Appendix A and includes:

- Precision - a measurement of mutual agreement among individual measurements of the same property usually under prescribed similar conditions, expressed generally in terms of the standard deviation;

- Accuracy- the degree of agreement between an observed value and an accepted reference value, accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations;
- Bias- the systematic or persistent distortion of a measurement process which causes errors in one direction. Estimates of the data quality will be calculated on the basis of single monitors and aggregated to all monitors.

18.1.6 Performance Evaluations (PE)

The PE is an assessment tool for the laboratory operations. The EPA's Contract laboratory for the UATMP creates "blind" samples and sends them periodically to the Ecology's laboratory. Upon receipt, the laboratory logs in the samples and performs the normal handling routines as any other sample. The PE is analyzed in accordance with the SOPs and QAPP. Then the results are reported to the EPA's Contract Laboratory Director. The Contract laboratory writes up a PE report and sends a copy of the results to Ecology and the EPA QA Office. Any results outside of the EPA's acceptance criteria are then noted in the PE report. Ecology has 120 days to address any deficiencies noted in the PE Report.

18.2 External Assessment Schedule

Table 18.1 Assessment Summary

Agency	Type of Assessment	Agency Assessed	Frequency
EPA - NAREL	TSA and PEs, round robin inter-laboratory samples	ERG	Annually
ERG	PEs	S/L/T agencies	Annually
OAQPS-EMAD	MSRs, TSAs	ERG, NAREL, EPA Regional and S/L/T agencies	As needed by EMAD determination
Regional Offices	Network Reviews	S/L/T agencies	Once every 5 years
Regional Offices	TSAs and IPAs	S/L/T agencies	Annually

19 Reports to Management

Important benefits of regular QA reports to management include the opportunity to alert the management of data quality problems, to propose viable solutions to problems, and to procure necessary additional resources. Management should not rely entirely upon the MSRs for their assessment of the data. The MSR only occur once every three years. Quality assessment, including the evaluation of the technical systems, the measurement of performance, and the assessment of data, is conducted to help insure that measurement results meet program objectives and to insure that necessary corrective actions are taken early, when they will be most effective.

Effective communication among all personnel is an integral part of a quality system. Regular, planned quality reporting provides a means for tracking the following:

- Adherence to scheduled delivery of data and reports;
- Documentation of deviations from approved QA and test plans, and the impact of these deviations on data quality;
- Analysis of the potential uncertainties in decisions based on the data.

19.1 Frequency, Content, and Distribution of Reports

Required reports to management for monitoring in general are discussed in various sections of 40 CFR Parts 53 and 58. Guidance for management report format and content are provided in guidance developed by EPA's Quality Assurance Division (QAD) and the Office of Air Quality Planning and Standards. These reports are described in the following subsections.

19.1.1 Toxics QA Annual Report

Periodic assessments of air toxics data are required to be reported to EPA (40 CFR 58 Appendix A, Section 1.4, revised July 18, 1997). The Toxics QA Annual Report, prepared the Toxics Air Monitoring Coordinator, will include quality information for each air toxic monitored in the network. Each section includes the following topics:

- Program overview and update;
- Quality objectives for measurement data;
- Data quality assessment.

For reporting air toxics measurement uncertainties, the Toxics QA Annual Report contains the following summary information:

- Flow Rate Audits;
- Collocated Samplers Audits using estimation of Precision;
- Laboratory audits which include "round-robin" cylinders that are shared among many laboratories;
- NPAP audits.

19.1.2 Technical System Audit Reports

Ecology performs Technical System Audits of the monitoring system. These reports will be filed and made available to EPA personnel during their technical systems audits.

External systems audits are conducted at least annually by the EPA Regional Office as required by 40 CFR Part 58. Further instructions are available from the EPA Regional QA Coordinator or the Systems Audit QA Coordinator, Office of Air Quality Planning and Standards, Emissions Monitoring and Analysis Division (MD-14), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

19.1.3 Response/Corrective Action Reports

The Data Disposition procedure will be followed whenever a problem is found such as a safety defect, an operational problem, or a failure to comply with procedures. A Data Disposition Report is one of the most important ongoing reports to management because it documents primary QA activities and provides valuable records of QA activities.

20 Data Verification and Validation

20.1 Data Verification Design

The primary purpose of this section is to describe the data verification procedures which are used by the AQP and WSU to process ambient air toxics data. The data review is performed as soon as possible after the data is collected, so that the questionable data can be checked by recalling information on unusual events and on meteorological conditions. Also, timely corrective actions are taken when indicated to minimize further generation of questionable data. Personnel performing data review are:

- Familiar with typical diurnal concentration variations (e.g., the time daily maximum concentrations occur and the interrelationship of pollutants.);
- Familiar with the type of instrument malfunctions which cause characteristic trace irregularities;
- Able to recognize that cyclical or repetitive variations may be caused by excessive line voltage or temperature variations.
- Able to identify when source activity can cause erroneous or non-representative measurements;
- Recognize that flow traces showing little or no activity often indicate flow problems, or sample line leaks.

A wide variety of information is used to validate air toxics data. Among them are the following, along with their uses:

- Multi-point Calibration Forms - the multipoint forms should be used to establish proper initial calibration and can be used to show changes in the calibration;
- Span Control Charts - these charts will be the most valuable tool in spotting data that is out of control limits;
- Site and Instrument Logs - because all station activities are noted in one or both of these logs, one can obtain a good picture of station operations by reading these logs;
- Data From Other Air Quality Stations - data from other air quality stations nearby can be compared between two stations to help the identification of invalid data;
- Blanks, Replicates and Spikes - these QC indicators can be used to ascertain whether sample handling or analysis is causing bias in the data set.

20.2 Data Review Testing and Procedures

Recently, WSU received a copy of the newly developed program VOCDat. This program was developed by EPA-OAQPS for PAMS data validation. However, WSU will apply this to the Organic Toxics data by using the following VOCDat tests:

20.2.1 Data Identification

Data with improper identification codes are useless. Three equally important identification fields which must be correct are time, location, parameter and sampler ID.

20.2.2. Unusual Event Review

Extrinsic events (e.g., construction activity, dust storms, unusual traffic volume, and traffic jams) can explain unusual data. This information may also be used to explain why no data are reported for a specified time interval, or it could be the basis for deleting data from a file for specific analytical purposes.

20.2.3. Relationship Checks

Toxics data sets contain many physically or chemically related parameters. These relations are routinely checked to ensure that the measured values on an individual parameter do not exceed the corresponding measured values of an aggregate parameter which includes the individual parameter. For example, benzene, toluene and xylene are mobile source driven. The relative concentrations are within +/- 10 ppbv, if these values are recorded at the same time and location. Data sets in which individual parameter values exceed the corresponding aggregate values are flagged for further investigation. Minor exceptions to allow for measurement system noise may be permitted in cases where the individual value is a large percentage of the aggregate value.

20.2.4. Review of Spikes, Blanks and Replicates

An additional check of the data set is to verify that the spikes, blanks and replicate samples have been reviewed. Generally, recovery of spikes in samples should be greater than 80%. Blanks should not be more than 3 times the MDL for any compound. The difference in concentration of replicates should be within +/- 10%. If any of these are outside of this boundary, then the reviewer will decide whether any of these results can or will invalidate a single run or batch.

20.2.5. Tests for Historical and Temporal Consistency

These tests check the consistency of the data set with respect to similar data recorded in the past. In particular these procedures will detect changes where each item is increased by a constant or by a multiplicative factor. Gross limit checks are useful in detecting data values that are either highly unlikely or considered impossible. The use of upper and lower 95% confidence limits is very useful in identifying outliers.

20.2.6 Pattern and Successive Difference Tests

These tests check data for pollutant behavior which has never or very rarely occurred in the past. Values representing pollutant behavior outside of these predetermined limits are then flagged for further investigation. Pattern tests place upper limits on:

- The individual concentration value (maximum-hour test);
- The difference in adjacent concentration values (adjacent hour test);
- The difference or percentage difference between a value and both of its adjacent values (spike test);
- The average of three or more consecutive values (consecutive value test).

20.3 Data Validation

The following quality assurance and data validation processes will provide for data that meets the Program's quality assurance criteria.

Station Operator's will be responsible for the first phase of data validation. They will screen, organize, and process the data and associated quality control information.

The laboratory will perform a full data validation of the analytical data to determine the bias and usability of the reported values. Data validations will be performed in accordance with the QA/QC requirements outlined in the QA Project Plan for Air Toxics, the specific Compendium Methods used, the Standard Operating Procedures of the laboratory, the Measurement Guidelines and the Validation Guidelines established by OAQPS for this program.

Prior to the Department officially reporting or using the data to make decisions concerning air quality, air pollution abatement, or control, the data will be reviewed and certified as valid by the Quality Assurance Coordinator.

In order for the data to be considered valid the following conditions must be satisfied:

- The air monitoring instrumentation must be calibrated and operated according to standard operating procedures that have been approved by the Quality Assurance Coordinator.
- The data must be bracketed by documented quality control checks which substantiate that it meets the criteria in Section 13 of this plan.

21 Reconciliation with Data Quality Objectives

21.1 Reconciling Results with DQOs

The DQOs for the air toxics monitoring network were developed in Section 6 and are stated below:

For the NATTS site, detect a percent difference change between successive three-year average concentration levels that are greater than or equal to 15 percent.

In addition, for the rest of the air toxics systems in the network:

Determine the highest concentrations expected to occur in the area covered by the network, i.e., to verify the spatial and temporal characteristics of HAPs.

The assessment procedure is used to determine whether the monitors and laboratory analyses are producing data that comply with the stated goals. Such an assessment is termed a Data Quality Assessment (DQA) and is thoroughly described in *EPA QA/G-9: Guidance for Data Quality Assessment*[1].

For the stated DQO, the assessment process will follow statistical routines. The following five steps identify how this will be achieved. Note that OAQPS will perform DQAs of the data from a national perspective. Therefore, Ecology will allow OAQPS to perform these assessments on their behalf. The DQAs that will be performed by the Ecology will pertain to the data collected at any other sites and the DQAs will pertain to answering the second statement.

21.2 Five Steps of DQA Process

The following will be performed as part of the DQA process:

- A review of the DQOs and sampling design;
- A preliminary data review;
- Summary statistics performed;
- Conclusions drawn from the data;
- An action plan based on conclusions from the DQA.